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(19)

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(54) COATED PEROXYGEN COMPOUNDS

(71) We, INTEROX CHEMICALS LIMITED, of Hanover House, 14 Hanover Square, London, W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the surface treatment of particulate peroxygen compounds, and to detergent blends containing such compounds.

Detergent blends have for many years contained a bleaching agent, often an active oxygen-containing compound such as sodium perborate tetrahydrate, or potassium peroxymonosulphate. In recent years two features have become apparent. The first feature has been the introduction of enzymes into heavy duty detergents in order to improve cold soaking performance, and cleansing of proteinaceous stains. Disadvantageously intimate mixture of enzymes with active-oxygen-containing compounds results in loss of activity of the enzyme during storage, particularly at elevated temperatures and relative humidities. The second feature has been a progressive increase in the proportion of bleaching agent in the detergent blend, from about 8—10% of about 10 years ago to about 20% or more in recent times, which has led to an increased use of mechanical techniques for handling the bleaching agent. Such techniques are abrasive, producing dust and fine particles in the detergent blend, so that when the blend is poured from a packet a cloud of dust particles is formed, which can be a nasal irritant.

It has been found that physical properties of solid peroxygen compounds (alternatively called herein percompounds of active-oxygen-containing compounds), may be modified by treating the surface of the percompound particles with an agent. It is believed that the surface treatment results in the agent forming a coating which at least partially covers the surface of the percompound particles.

According to the present invention there is provided a solid percompound coated with a coating agent comprising a condensation product of at least one long chain fatty acid as defined herein and a poly(alkylene glycol) or a poly(alkylene glycol) terminally substituted by one or two amine groups. Reference hereinafter to a poly(alkylene glycol) includes mutatis mutandis a reference to a corresponding poly(alkylene glycol) in which one or both terminal hydroxy groups have been replaced by amine groups. Suitably the esters and amides are derivatives of poly(ethylene glycol) (P.E.G.), the P.E.G. moiety having an average molecular weight suitably of at least 200, desirably at least 250 and preferably at least about 300. Desirably the P.E.G. moiety has an average molecular weight of below about 2000, advantageously below about 1500 and preferably below about 1000. In particularly preferred embodiments of the invention the average molecular weight of the P.E.G. moiety may be about 300, about 400, about 600, about 700 or about 1000, being in the range of 250 to 1500.

In other embodiments the poly(alkylene glycol) can comprise poly(propylene glycol) (P.P.G.) having an average molecular weight of at least about 1000, preferably from about 1000 to 2000, or contain the P.P.G. in for example a P.E.G./P.P.G. copolymer having a high P.E.G. content of about 50% or more.

Suitably the coating agent is a mono- or di- fatty acid condensate of a poly(alkylene glycol), or optionally as stated before the corresponding amine terminated poly(alkylene glycol). The or each fatty acid residue, by which term we mean a residue of a monocarboxylic acid containing at least 8 carbon

atoms in an aliphatic chain, desirably contains from 8 to 26, preferably 10 to 24, particularly 12 to 22 carbon atoms and may be saturated on unsaturated. Examples of fatty acids include lauric, stearic and oleic acid and fatty acids derived from coconut oil, castor oil, and groundnut oil, and hydrogenated derivatives thereof.

Other suitable saturated fatty acids comprise myristic, palmitic, arachidic and behenic acid, otherwise known respectively as tetradecenoic, hexadecenoic, eicosanoic and docosanoic acids and suitable unsaturated acids include hexadecenoic acids, hexadecynoic acids, other octadecenoic acids, octadecynoic acids and docosenoic acids, examples of which are hypogeic, erucic and stearolic acid. Preferably the fatty acid residue is saturated because condensates of saturated fatty acids and a poly(alkylene glycol) tend to have higher melting points than their corresponding unsaturated condensates.

Preferably the fatty acid and poly(alkylene glycol) are so chosen that the coating agent has a melting point of at least 25°C, particularly of at least 30°C, and desirably melts at up to about 50°C.

Particularly suitably the coating agent is a mono derivative, especially the monoester rather than the monoamide. The coating agent, such as the condensation product of P.E.G., optionally amine terminated, and the fatty acid preferably has an average molecular weight of from 300 to 1700, and coating agents having such a preferable molecular weight may be produced by condensing for example, the above-mentioned preferred P.E.G. moieties with any of the fatty acids herein described.

Suitably the peroxygen compound is coated with at least 0.1%, preferably at least 0.2% of coating agent. If the coating agent melts at up to 25°C, desirably no more than 5% by weight is used, because percompounds, other than perborate monohydrate, when coated with more than about 5% of such a coating agent tend to suffer caking and poor flow properties. Perborate monohydrate may conveniently be treated with up to 20%. If the coating agent melts at above 25°C, desirably no more than 20%, conveniently no more than 15% by weight is used, because use of more than about 20% renders the coated percompound more expensive and may increase the tendency for dust particles to be formed during handling.

Suitably the peroxygen compound in any particulate inorganic or organic compound which contains active oxygen, thereby having bleaching properties under detergent conditions. Examples of the inorganic peroxygen compound are alkali metal perborate tetrahydrates, monohydrates and trihydrates, alkali metal permonosulphates, and adducts of alkali metal salts with hydrogen peroxide such as alkali metal carbonates, tripolyphosphate and pyrophosphates for example, in each case particularly the sodium salt. Examples of organic peroxygen compounds include solid organic peracids, such as peroxybenzoic acid, preferably having a melting point of 50°C or higher, such as peroxyphthalic acid or esters of organic peracids, and diacyl peroxides.

It is to be understood that preferred coating agents for organic peroxygen compounds generally speaking may have a balance between the hydrophilic poly(alkylene glycol) moiety and the hydrophobic fatty acid residue different from that in the preferred coating agents for inorganic peroxygen compounds, and that individual percompounds, either organic or inorganic, may require different coating agents or amounts of coating agent to achieve the most desirable modification of the physical properties of that percompound.

The coating may be applied by conventional coating techniques. In one method the coating agent at a temperature above its melting point is introduced, for example by pouring or spraying into a bed of peroxygen compound particles maintained at that temperature, agitated mechanically in, for example, a Lodige-Morton mixer and then allowed to cool. In a second method the coating agent, at a temperature above its melting point, is sprayed onto peroxygen compounds agitated in a fluidised bed at that temperature. Alternatively the fluidised bed may be unheated. In a third method the coating agent is dissolved in a solvent, preferably having a low volatility such as a lower aliphatic alcohol such as ethanol, and sprayed onto peroxygen compound particles agitated in a fluidised bed, the bed being supplied with sufficient hot air to evaporate off the solvent. In a fourth method the coating agent is dissolved in a solvent, particles of peroxygen compound are immersed in the solution and an antisolvent is added, thereby causing the coating agent to be coacervated upon the particles, which are then filtered off and dried. Alternatively, the coating agent may be precipitated onto the particles by contacting a saturated solution of the agent at a high temperature with the particles and then allowing the solution to cool.

Application of the same proportion of coating agent using different methods to particles of peroxygen compound having a certain set of physical characteristics may produce products having differing packet stabilities.

Particles having any shape or size may be coated but preferably, as high a proportion as possible of the particles, in a single batch to be coated, have a similar surface area/volume ratio, so that the coated product has substantially constant packet stabilities. A

particle having a high particle diameter has a low surface area/volume ratio and for any given particle diameter, a spherical particle has the lowest area/volume ratio. Preferably the particles are substantially spherical, suitably having a particle diameter of from approximately 75μ to about 1000μ.

The particles to be coated may have been produced by any suitable process, such as a crystallisation process or fluidised bed process, and may, or may not, have been classified.

The particles may be coated by more than one coating of the coating agent, the coating being the same compound or different. Alternatively the particles may be coated with one or more layers of the coating agent described herein and one or more layers of the coating agent described in British Patent Specification No. 1370626.

In detergent blends containing both an enzyme component and an active oxygen-containing compound in an intimate mixture the enzyme component loses its activity at a reduced rate when the active oxygen-containing compound is coated according to the present invention. The coating would appear to act as a physical barrier preventing intimate contact of the peroxygen compound particles with the enzyme particles. The coating agents described herein are compatible both with the peroxygen compound and with the enzyme.

Peroxygen compounds when stored under humid conditions in intimate mixture with other components of present-day detergent blends suffer decomposition and thus loss of active oxygen and bleaching power. The rate of decomposition varies from peroxygen compound to peroxygen compound, sodium perborate tetrahydrate having a slow rate, and sodium carbonate perhydrate having a much faster rate. Under conditions of storage experienced in packets for example during summer months in warehouses of Mediterranean countries, the high temperatures of about 30°C and humidities of about 70 and 80% induce a significant rate of decomposition especially for sodium percarbonate. The peroxygen compound coated according to the present invention suffers under similar conditions significantly less decomposition than does the uncoated peroxygen compound. The advantage is particularly noticeable under the stringent conditions described above, and for the more easily decomposable peroxygen compounds such as adducts of alkali metal salts with hydrogen peroxide, e.g. sodium carbonate perhydrate and sodium pyrophosphate perhydrate, alkali metal peroxymonosulphates, e.g. potassium peroxymonosulphate, and many organic peroxy acids, peroxy esters and diacyl peroxides. It is believed that esters of organic peroxy acids and diacyl peroxides may be hydrolysed to peroxyacids (which may then decompose releasing active hydrogen) at a slower rate than corresponding uncoated esters of peroxyacids and diacyl peroxides.

In comparison with uncoated compounds, peroxygen compounds coated with small amounts of particularly preferred coating agents e.g. the monocondensation product of PEG 300 and stearic acid suffer less particle breakdown and have a decreased tendency to form dust, as may be measured using conventional attrition tests. Such particularly preferred coated peroxygen compounds are suitable for use in mechanical bulk handling processes now used in the preparation of detergent blends. Thus, although advantages of coating the peroxygen compound are more noticeable when the detergent blend contains enzymes, it is still advantageous to coat the peroxygen compounds even when the detergent blend is enzyme-free.

They are also provided according to the present invention detergent blends containing one or more peroxygen compounds coated in a coating agent herein described.

Detergent blends are often designed so as to have an active oxygen content of from 0.5% to 3% or even 4% by weight, based on the blend, and this content in the blend can be achieved by mixing the appropriate quantity of peroxygen compound with a base detergent composition, it being understood that the appropriate quantity will vary from peroxygen compound to peroxygen compound and be inversely proportional to the active-oxygen content of the pure peroxygen compound. For example sodium perborate tetrahydrate has an active oxygen content of about 10% and sodium carbonate perhydrate about 14%. Hence to achieve an active oxygen content of 2% requires about 20% of sodium perborate tetrahydrate and only about 14% of sodium carbonate perhydrate (percentages by weight based on the detergent blend). Other components which may be present in the detergent blend include surface active agents, eg. fatty acids or alkali metal salts thereof, alkyl sulphonates, alkylated aryl sulphonates, sulphated aliphatic olefins and sulphated aliphatic amide condensation compounds, organic or inorganic builders eg. sodium tripolyphosphate, enzymse, sodium sulphate and sodium silicate. Suitable enzymes are sold by respectively Novo Industri, Royal Netherlands Fermentation Industrie, Kali Chemie and Pfizer, under the Trade Marks NOVOLASE, MAXATASE, OPTIMASE, and SUPERASE.

Certain embodiments of the invention will now be described more fully by way of Example only. In the Examples sodium carbonate perhydrate (percarbonate) was produced by a conventional crystallisation process and had a particle size range of from

75μ to 1000μ and the sodium perborate tetrahydrate (perborate) had a particle size range of 75μ to 1000μ.

Example 1.

In this Example percarbonate was coated with a coating agent comprising 5% by weight (except where indicated) based on the coated compound of the condensation product shown in Table 1 by melting the coating agent, fluidising the particles of percarbonate in a bed maintained at about 35°—45°C, spraying sufficient of the coating agent onto the particles, and then allowing the particles to cool. The coated or uncoated percarbonate was then mixed intimately with an enzyme-free or enzyme-containing base detergent composition having components falling within the ranges (based by weight on the base detergent) of

	Enzyme-free	Containing 0.5% Enzyme
sodium dodecyl benzene sulphonate	25—30%	25—30%
sodium tripolyphosphate	35—40%	25—30%
sodium silicate	10—15%	5—10%
sodium sulphate	10—15%	20—30%
water and additives	to 100%	to 100%

so as to give an active oxygen content of approximately 2% by weight based on the detergent blend, the precise percentage being determined as below. The detergent blends were then stored in conventional wax laminated cardboard containers of low permeability under the conditions shown in Table 1. The compositions were tested for active oxygen content by dissolving completely a known weight of detergent in dilute aqueous sulphuric acid and titrating the resulting solution against a standardised potassium permangate solution at the times indicated in Table 1. The figures given indicated the extent to which the active oxygen content of the percarbonate had been lost.

The storage conditions are denoted by A, B, C, D in which A and B are at 28°C and 70% RH, C and D are at 32°C and 80% RH, A and C are enzyme-free, and B and D are in the presence of the proteinaceous enzyme.

TABLE 1

Condensation Product of	Storage Conditions	% of Active Oxygen Lost Time in Storage (Weeks) 0	2	4	8	12	20
Uncoated	A	0	2	0	10	14	31
	B	0	11	7	43	64	82
	C	0	3	7	13	34	—
	D	0	14	24	55	88	93
PEG 300 Stearic Acid	A	0	0	4	6	10	21
	B	0	0	11	18	28	62
PEG 1000 Stearic Acid	A	0	0	3	0	9	5
	B	0	0	1	6	15	21
	C	0	0	1	3	8	15
	D	0	0	2	13	21	37
PEG 1000 Stearic Acid (coating of 3% by weight)	A	0	1	4	7	10	18
PEG 1000 Oleic Acid	A	0	0	4	9	12	25
	B	0	1	7	18	35	70
	C	0	0	6	14	30	39
	D	0	5	18	27	60	81
PEG 1000 Lauric Acid	A	0	0	4	7	9	25
	B	0	0	6	17	34	68
	C	0	1	5	8	20	28
	D	0	4	15	23	41	49

Example 2.

Perborate or percarbonate, was coated with the coating agent and the amount shown in Tables 2 and 3, by the method described in Example 1. Coated or uncoated perborate or percarbonate was then thoroughly mixed with the enzyme-containing base detergent as described in Example 1 so as to give products having an available oxygen content of approximately 2% by weight based on the product. Each product contained approximately 0.5% by weight based on the product of an active enzyme, bacillus subtilis sold by Novo Industri of Denmark under the Trade

name ALCALASE, the enzyme being supported on tripoly phosphates. The product was then stored in conventional wax-laminated detergent packets of low permeability or packets of zero permeability at 28°C and 70% relative humidity. The activity of the enzyme was tested regularly by the method described by Y. Lin, G. E. Means and R. E. Feeney in an article entitled the Action of Proteolytic Enzymes on N, N Dimethyl Proteins, published in Volume 244, No. 4, the February 1969 issue of the Journal of Biological Chemistry pages 789—793. The time taken for the activity of the enzyme to fall to half its original value is shown in Tables 2 and 3.

TABLE 2

Low Permeability Packages			
Amount	Coating Agent Condensation Product of	Enzyme Half Life (days) Perborate	Percarbonate
—	—	22	13
—	—	27	14
1%	PEG 1000 Stearic Acid	21	15
1.5%	PEG 1000 Stearic Acid	—	14
3%	PEG 1000 Stearic Acid	29	19
5%	PEG 1000 Stearic Acid	40	38
1%	PEG 300 Stearic Acid	28	—
3%	PEG 300 Stearic Acid	37	—
5%	PEG 300 Stearic Acid	50	37
5%	PEG 1000 Oleic Acid	35	26
25%	PEG 1000 Oleic Acid	42	—
5%	PEG 1000 Lauric Acid	33	27
25%	PEG 1000 Lauric Acid	41	—
5%	PEG 300 Distearic Acid	37	—

TABLE 3

Zero Permeability Packages			
Amount	Coating Agent Condensation Product of	Enzyme Half Life (days) Perborate	Percarbonate
—	—	30	13
—	—	35	15
1%	PEG 1000 Stearic Acid	44	—
5%	PEG 1000 Stearic Acid	63	37
1%	PEG 300 Stearic Acid	61	—
5%	PEG 300 Stearic Acid	>100	28
1%	PEG 1000 Oleic Acid	37	—
5%	PEG 1000 Oleic Acid	42	31
1%	PEG 1000 Lauric Acid	40	—
5%	PEG 1000 Lauric Acid	45	31

From Tables 2 and 3 it can be seen that increasing the amount of agent generally increased the half life of the enzyme, and that the most effective of the coating agents described in this Example was the condensation product of PEG 300 and stearic acid.

Example 3.

In this Example the attrition resistance of coated and uncoated sodium perborate tetrahydrate and sodium percarbonate was compared.

Sodium percarbonate and sodium perborate tetrahydrate were coated by a process according to Example 1, using the coating agents and amount shown in Table 4. The attrition resistance is expressed in terms of % friability, the lower the friability, the better the attrition resistance.

The friability was measured using a standard test procedure. A sample was divided to give portions each of approximately 50 g by weight. A first portion was weighed accurately (W) and sieved. Weight A passed through a 150μ (100 mesh) sieve. A second portion of weight B was placed in the attrition chamber of apparatus comprising a gas cylinder connecting through a pressure regulator to a vertical attrition chamber equipped with a base plate having a single hole of 0.016 inches drilled centrally. The gas flow was regulated to between 6.75 and 7.251 N per minute (i.e. normalised to 0°C and a pressure of 760 mm of mercury) at a delivery pressure of 42—48 p.s.i. (approx. 2.95 to 3.37 kg/cm^2) for 10 minutes. The portion was then sieved, the fraction passing through the 150μ sieve discarded, and the remainder weighted (C).

The % friability was given by the formula:

$$100\left[\frac{B-C}{B}-\frac{A}{W}\right]\%$$

TABLE 4

Amount	Coating Agent Condensation Product of	Friability % of Perborate	Percarbonate
–	–	15.9	4.7
1%	PEG 300 Stearic Acid	12.1	3.1
3%	PEG 300 Stearic Acid	6.2	1.4
5%	PEG 300 Stearic Acid	0.3	0.9
5%	PEG 1000 Stearic Acid	0.8	1.5
5%	PEG 1000 Oleic Acid	1.0	1.0
5%	PEG 1000 Lauric Acid	1.3	1.2

It may be seen from the above that the attrition resistance of both percarbonate and perborate was improved by coating using the coating agents and amounts above exemplified.

WHAT WE CLAIM IS:—

1. A solid percompound coated with a coating agent comprising a condensation product of at least one long chain fatty acid as herein defined and a poly(alkylene glycol) or a poly(alkylene glycol) terminally substituted by one or two amine groups.

2. A coated percompound as claimed in claim 1 wherein the poly(alkylene glycol) moiety of the condensation product is a polyethylene glycol moiety.

3. A coated percompound as claimed in claim 2 wherein the polyethylene glycol moiety has an average molecular weight of from 200 to 2000.

4. A coated percompound as claimed in claim 2 wherein the polyethylene glycol moiety has an average molecular weight of from 300 to 1000.

5. A coated percompound as claimed in claim 1 wherein the poly(alkylene glycol) moiety comprises a polypropylene glycol moiety having a molecular weight of about 1000 to 2000.

6. A coated percompound as claimed in claim 2 wherein the coating agent has an average molecular weight of from 300 to 1700.

7. A coated percompound as claimed in any previous claim wherein the or each fatty acid contains from 8 to 26 carbon atoms.

8. A coated percompound as claimed in claim 7 wherein the or each fatty acid contains from 12 to 22 carbon atoms.

9. A coated percompound as claimed in claim 7 or claim 8 wherein the or each fatty acid is saturated.

10. A coated percompound as claimed in claim 6 wherein the coating agent has a melting point of at least 30°C.

11. A coated percompound as claimed in claim 7 wherein the coating agent is a mono condensation product of polyethylene glycol having an average molecular weight of from 250 to 1500 and stearic acid.

12. A coated percompound as claimed in any previous claim wherein the percompound is coated with from 0.1% to 20% by weight of coating agent having a melting point above 25°C.

13. A coated percompound as claimed in any one of claims 1 to 11 wherein from 0.2% to 5% by weight of coating agent having a melting point of up to 25°C is used.

14. A coated percompound as claimed in claim 1 and substantially as described herein with respect to any of the Examples.

15. A process for coating a solid percompound comprising contacting the percompound with a coating agent as claimed in any previous claim.

16. A process for coating percompound as claimed in claim 15 and substantially as described herein.

17. A detergent blend containing a percompound as claimed in any one of claims 1 to 14.

18. A detergent blend as claimed in claim 17 containing an enzyme.

19. A detergent blend as claimed in claim 17 or claim 18 and substantially as described herein.

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